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Surface Morphology and Microstructure of Zinc Deposit From Imidazole with Zinc Chloride Low Temperature Molten Salt Electrolyte in The Presence of Aluminium Chloride

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ABSTRACT

Low temperature molten salts have variety of applications in organic synthesis, catalytic processing, batteries and electrode position due to their air and water stability. They have wide potential window for their applications in voltage and temperature and hence there is a possibility to deposit metals which could not be deposited from aqueous electrolytes. Our aim and scope of our research was to deposit zinc from low temperature molten salt electrolyte (LTMS) containing zinc salt in the presence of aluminium chloride at different current densities and to qualify the nature of deposits. We could identify the effect of current density on the deposit at low temperature molten salt electrolyte by analysing the nature of deposits using different instrumental techniques. Compact, adherent, dense fine grained deposits of zinc with average grain size of 40-150 nm could be obtained from low temperature molten salt electrolyte. (LTMS)

Keywords: Surface morphology, Crystallographic orientation, Topography, Surface roughness , Zinc electrode posit, Zinc chloride, Imidazole, LTMS

INTRODUCTION: Mechanical, Physical, and Chemical properties of the nano crystalline materials are superior than conventional polycrystalline materials and such zinc coatings are higher corrosion resistance and hardness than the polycrystalline coatings. Zinc deposits of nano laminated structures were produced from an acid sulphate and chloride electrolyte by applying direct current (DC). Pulse electro deposition usually allows higher current density and it yields zinc deposits with a finer grain size and shows more homogeneity in surface appearance than the deposits obtained from DC. It is reported that high current density induces increased cathode over potential and nucleation rate for the formation of finer grains. Such zinc deposits were obtained from an aqueous-chloride as well as from a sulfate bath. In Present study, under normal conditions electrodeposits could be obtained in the range of nano to sub micrometers from low temperature molten salt which is a good alternative to hazardous cyanide plating electrolyte. [1-15]. The impact of current density on the surface morphology and structure of electrodeposits from Imidazole with $alcl_3$ and zinc chloride low temperature molten salt electrolyte were characterized by using SEM, EDAX, XRD, AFM.

EXPERIMENTAL: Zinc from imidazole with zinc chloride and alcl3 electrolyte (LTMS) was electrodeposited at different current densities from the range of 1 A/dm^2 to 9 A/dm^2 at the temperature of 100°C. Platinum was used as anode . Copper was used as cathode. 1cm2 of copper was cleaned with Trichloroethylene and then with cleaning powder. After pre treating by etching, the copper substrate was electrodeposited from low temperature molten salt electrolyte in optimized mole ratio of imidazole, zinc chloride with $alcl_{3\,,}$ using various current densities of 1 to 9 A/dm^2 and keeping the temperature of about 100°C. Surface morphology, crystallographic orientation and grain structure of zinc deposited samples were analysed by using SEM, EDAX, XRD, AFM and the results were evaluated.

RESULTS AND DISCUSSION:

SEM: Zinc electrodeposits from LTMS was characterised using Scanning Electron Microscopy (SEM, HITACHI, JAPAN). Deposit at current density of 1A/dm^2 show grain like compact uniform, adherent with homogeneity of nano laminated crystals were seen as shown in fig.1 Deposit at current density of 2A/dm^2 shows petals like structure due to its aluminium inclusion as a impurity as shown in fig.2 Deposit at 3A/dm^2 show uniform granular like structures as shown in fig.3. Deposit at 5A/dm^2 show hcp structure of zinc predominately as shown in fig.4. At current density 2A/dm2 aluminium act as impurity and it deposited from aluminium chloride imidazloe complex and show petals like structure, while at 5A/dm2 zinc preferentially deposited and it show its hcp structure of zinc. Inclusion of aluminium favours at lower current density while zinc deposited at vice versa.

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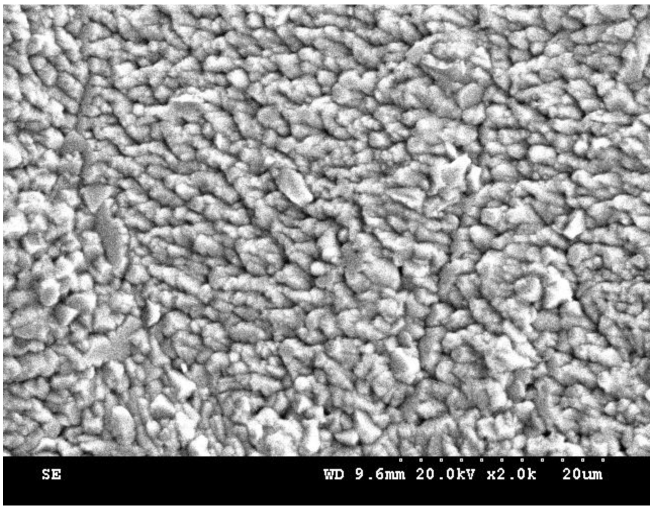


Fig. 1(a) SEM at 1 a/dm^2

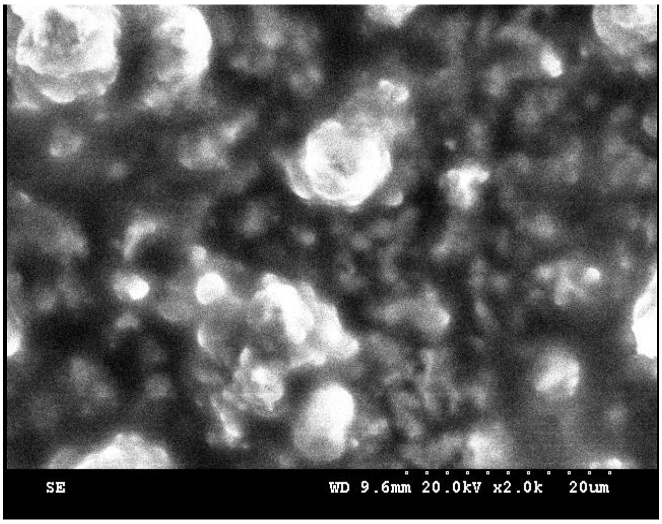


Fig. 1(b) SEM at 2 a/dm^2

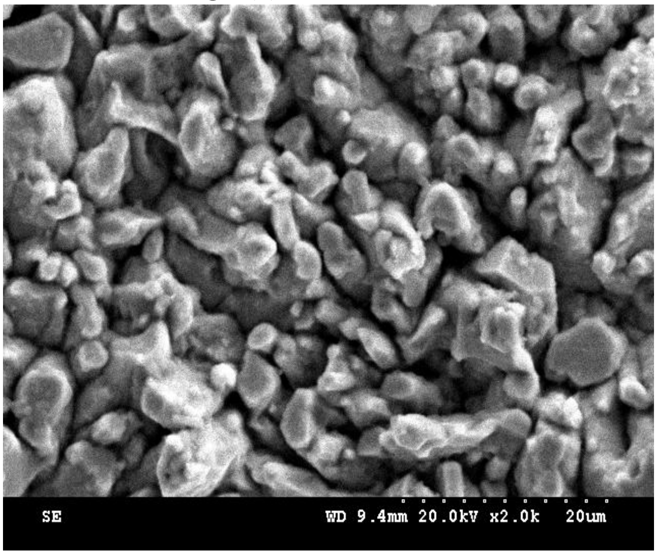


Fig. 1(c) SEM at 3 a/dm^2

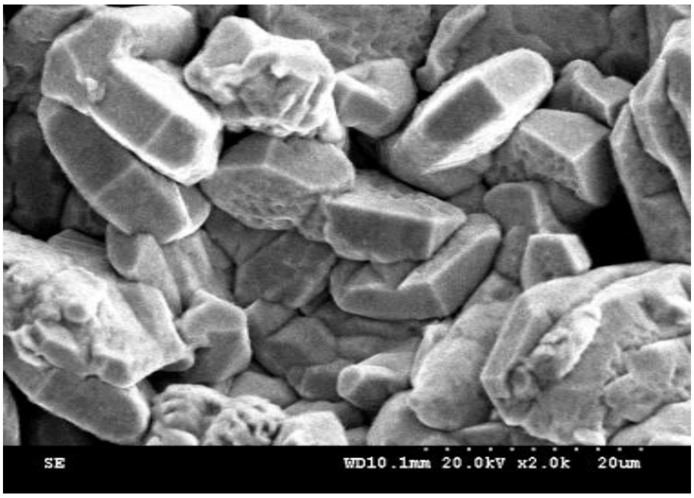
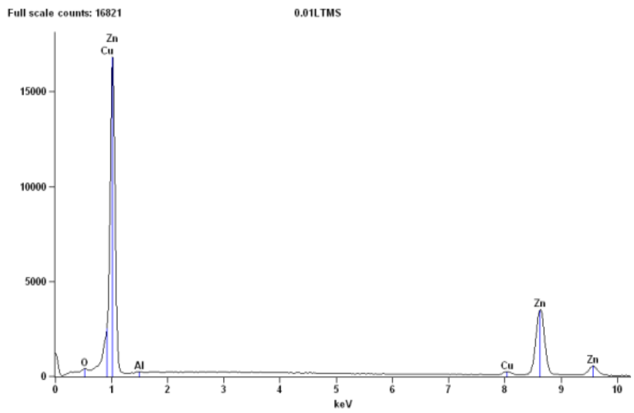


Fig. 1(d) SEM at 5 a/dm^2

EDAX: EDAX analysis of zinc deposits at different current densities are as shown below (fig. 2-5). Zinc deposition favours at higher percentages at higher current density while aluminium deposition favours at lower current density. As per EDAX analysis (fig.2) at 1A/dm2 it shows higher percentages of aluminium as compared to other current densities and it has been integrated with zinc as grain like structures as in SEM. Fig.1(a). At 2A/dm2 oxygen inclusion is higher and the aluminium inclusion is very less at 2A/dm2 than 1a/dm2, 3A/dm2 and its represented as represented in peak of EDAX (Fig.3) as a thin film of aluminium oxide over the surface of zinc deposits and it correlates petals like structure on the zinc crystals as shown in SEM fig .1(b). At 3 A/dm2 aluminium inclusion is slightly higher in EDAX (Fig.4) and integrated as granular like structure as in SEM Fig.1(c). At 5 A/dm2 the inclusion of aluminium is very less than other current densities (fig.5) and hence the predominant structure of hcp crystals of zinc was seen as in SEM fig .1(d).



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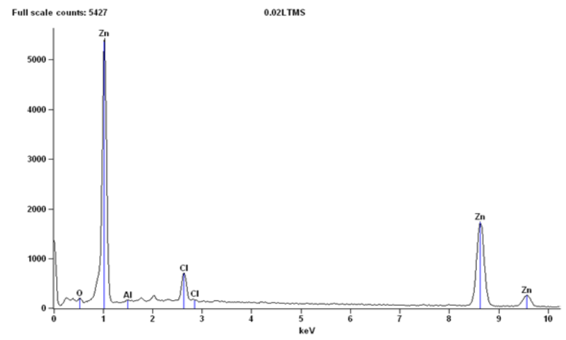
Element	*Net Counts*	*Weight %*	*Atom %*
Al	1176	**0.884**	1.93
Zn	69768	**99.116**	89.03
Total		100.00	100.00

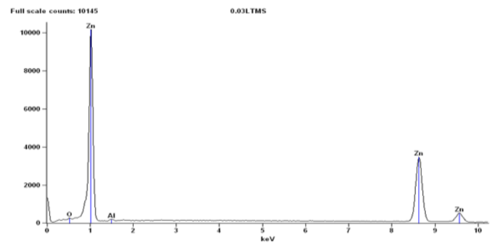
Fig. 2 EDAX analysis for zinc deposits obtained at 1A/dm^2



Quantitative Results 0.02LTMS

Element	*Net Counts*	*Weight %*	*Atom %*
Al	408	0.61	1.21
Zn	33499	99.39	81.42
Total		100.00	100.00

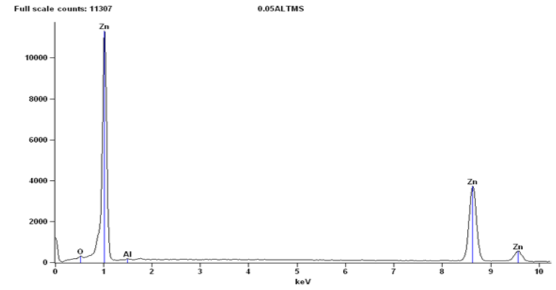
Fig. 3 EDAX analysis for zinc deposits obtained at 2A/dm^2



Quantitative Results 0.03LTMS

Element	*Net Counts*	*Weight %*	*Atom %*
Al	909	0.715	1.69
Zn	67014	99.285	96.02
Total		100.00	100.00

Fig. 4 EDAX analysis for zinc deposits obtained at 3A/dm^2



Quantitative Results 0.05ALTMS

Element	*Net Counts*	*Weight %*	*Atom %*
Al	574	0.426	0.97
Zn	72239	99.574	94.36
Total		100.00	100.00

Fig. 5 EDAX analysis for zinc deposits obtained at 5A/dm^2

XRD: X-ray diffraction (XRD) measurements of the zinc deposition the presence of aluminium were performed using a diffractometer (PANANALYTICAL, X'PERT PRO, Netherlands) and XRD pattern analysis of zinc deposit at different current densities are shown in figures 6-9. There is some marginal difference in peak but pattern was more are less same at different current densities. The basal plane of zinc (002) was observed by higher intensity peak. From the basal plane of zinc (002), the parallel planes of (101),(102) and pyramidal planes of (110),(112),(202) with lesser peak intensities than (002) plane of zinc on cu (200) substrate was observed. The high intensity peak of basal plane (002) indicates its compact dense nature of deposit and it denotes its nano crystallinity at lower current density. At lower current density to higher current density the nucleation growth deposit difference occurs from epitaxial to non epitaxial over the copper substrate and its indicated by its structure in SEM as well as the grain size calculated [16-21]. The crystallite size D was calculated from the peak width at half of the maximum peak intensity b by the Scherrer's formula and the average grain size is 40nm-150nm i.e; nanometers to submicrometers. The inclusion of aluminium as minor elements as aluminium i.e: xrd Plane (400) as well as aluminium oxide and it was represented in the xrd plane of (306).

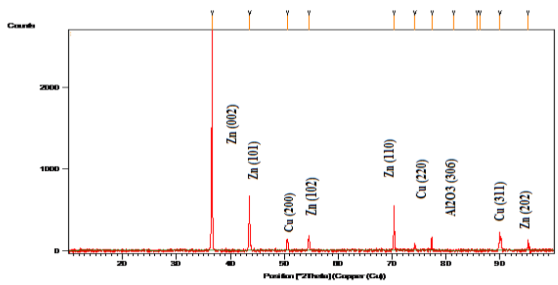


Fig: 6 XRD Pattern of LTMS Zinc with $AlCl_3$ at 1 A/dm^2

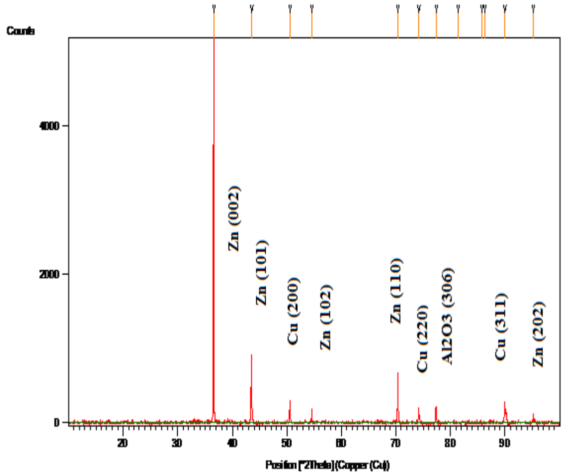


Fig: 7 XRD Pattern of LTMS Zinc with $AlCl_3$ at 2 A/dm^2

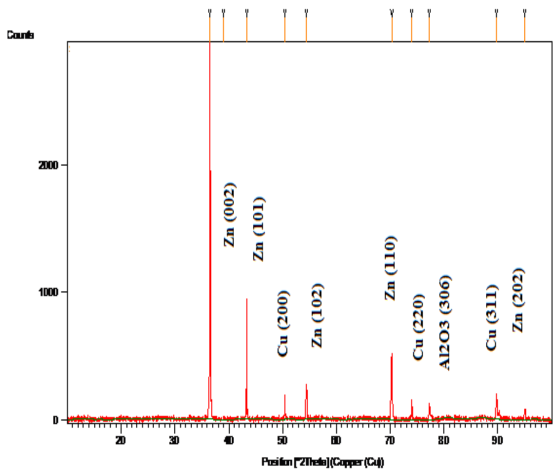


Fig: 8 XRD Pattern of LTMS Zinc with $AlCl_3$ at 3A/dm^2

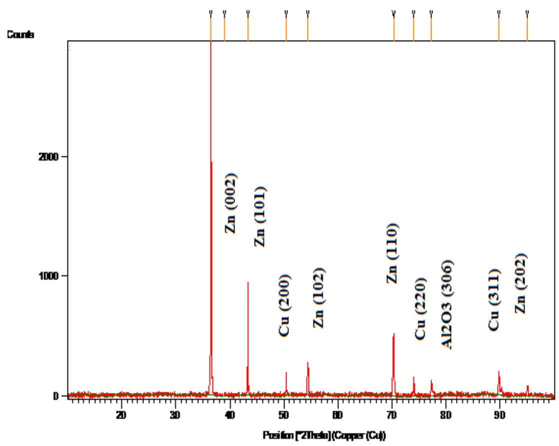


Fig: 9 XRD Pattern of LTMS Zinc with $AlCl_3$ at 5 A/dm^2

Pos. [°2Th.]	Height	FWHM	d-spacing	Rel. Int.
36.6202	2670.80	0.1428	2.45194	100.00
43.5488	835.88	0.1224	2.07654	31.30
50.6309	215.77	0.2856	1.80144	8.08
54.6272	260.16	0.2856	1.67872	9.74
70.3742	528.27	0.1428	1.33675	19.78
74.2709	76.63	0.2856	1.27596	2.87
77.3621	165.33	0.2040	1.23251	6.19
81.3722	9.89	0.2448	1.18160	0.37
85.7041	12.52	0.3264	1.13261	0.47
86.2606	6.49	0.2448	1.12673	0.24
90.9968	190.57	0.4896	1.08940	7.14
95.1438	95.98	0.2448	1.04359	3.59

AFM: Surface topography was analysed using AFM (Molecular imaging scanning probe microscope, Model:PICOSPM,US) and it shows nanocrystalline at 1A/dm2 and the crystalline size is in the range ~40-50 nanometres(scanned area 1micrometer) and the stucture is integrated grain like structure of zinc with aluminium and at 2a/dm2 ~200 nanometers(scanned area 3micrometer) and the structure is nodular structure(2D) and closely packed columnar structure (3D) due to the aluminium oxide as a thin film over the zinc deposit. and at 5 a/ dm2 ~100 nanometers(scanned area 1micrometer) and the crystallites are predominantly hexagonal platelet shaped hcp crystal structure of predominiated zinc. The topography at diffent current densities at 2D and at 3D are shown infigures 10(a),10(b),11(a),11(b,c),12(a),12(b).

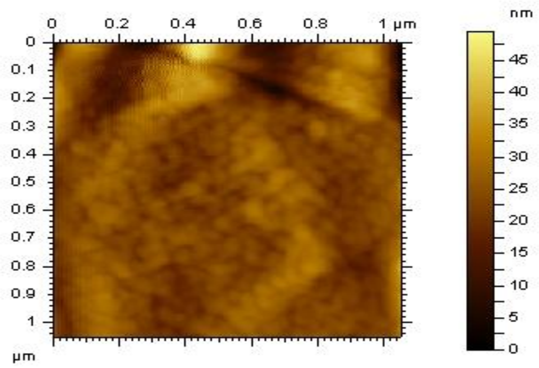


FIG.10(a)

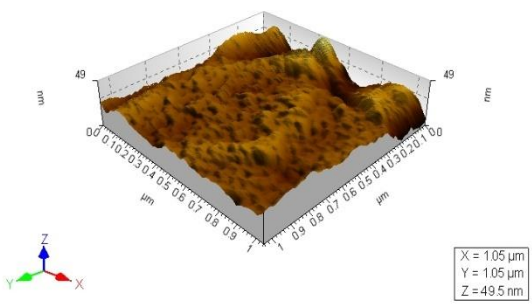


FIG.10(b)

FIG.10(a) AFM structure of zinc deposit from Imidazole with zinc chloride and aluminium chloride at 1 A/dm^2 at 2D and 10(b) at 3D

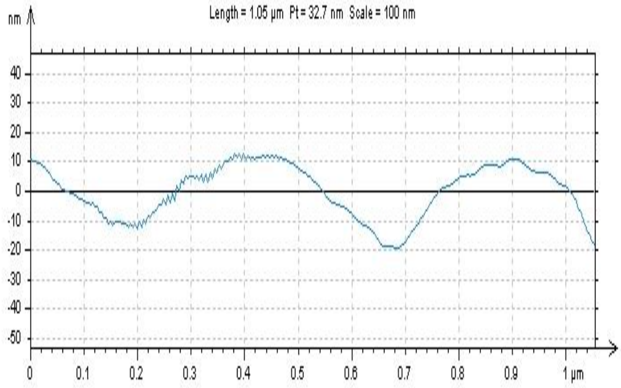


FIG.10(c) AFM - crystalline depth profile of zinc deposit from LTMS at 1A/dm2

The average roughness profile (Ra) at 1 a/dm2 is 1.80 nanometres and the Root mean square deviation of the roughness profile (RMS) is 2.20 nano meters. The crystalline depth profile of zinc deposit from LTMS in the presence of aluminium chloride at 1A/dm2 is shown in fig.10 (c).

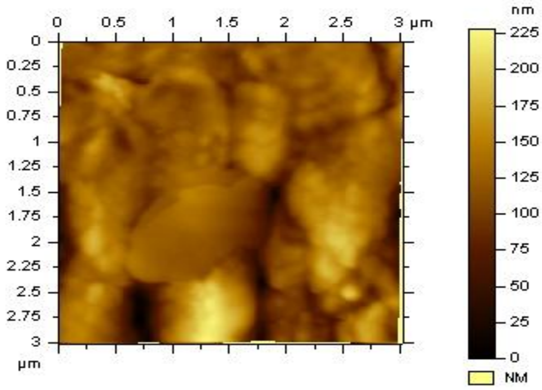


FIG.11(a)

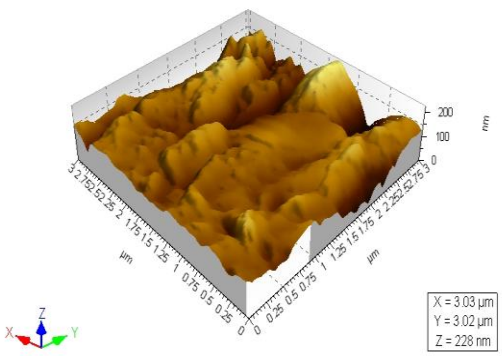


FIG.11(b)

FIG.11(a) AFM structure of zinc deposit from Imidazole with zinc chloride and aluminium chloride at 2 A/dm^2 at 2D and 11(b,c) at 3D

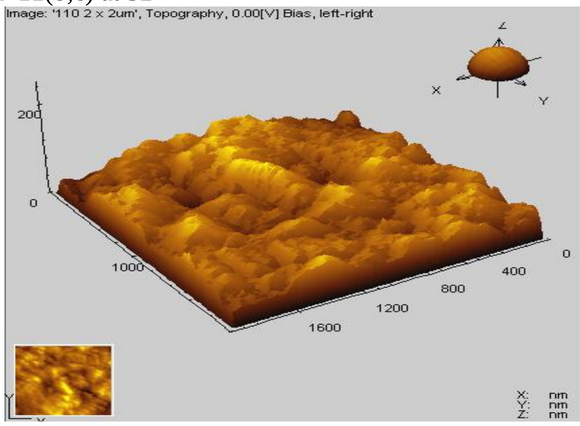


FIG.11(c)

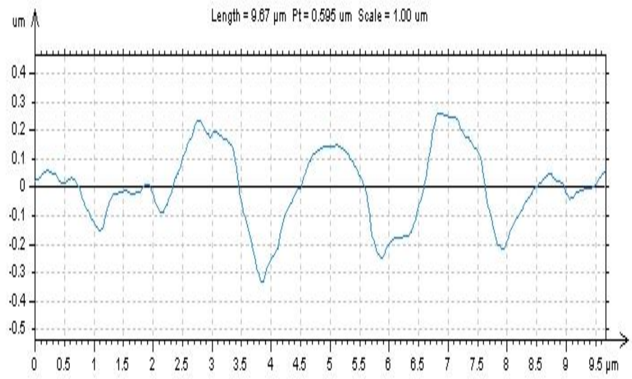


FIG. 11(d) AFM - Crystalline Depth profile of zinc deposit from LTMS at 2A/dm2

The average roughness profile (Ra) at 2 a/dm2 is 7.55 nanometres and the Root mean square deviation of the roughness profile (RMS) is 10.5 nano meters. The crystalline depth profile of zinc deposit from LTMS in the presence of aluminium chloride at 1A/dm2 is shown in fig.11 (d).

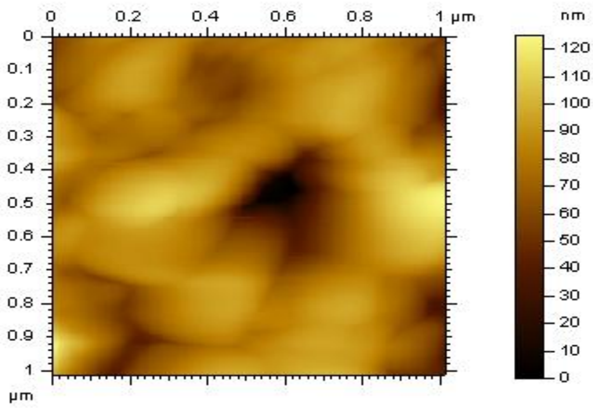


FIG.12(a)

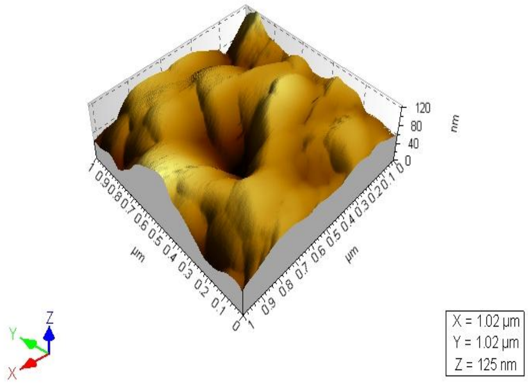


FIG.12(b)

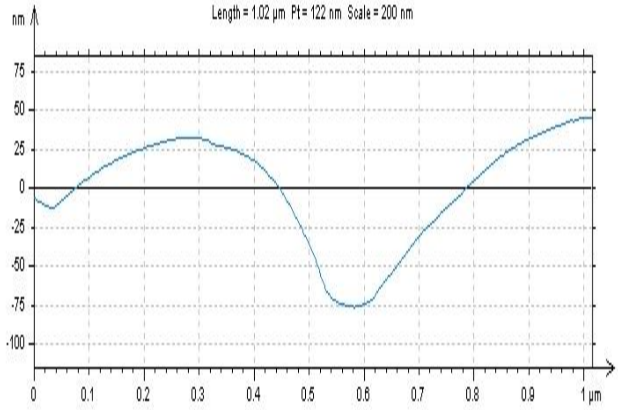


FIG.12(c) AFM – Crystalline depth profile of zinc deposits from LTMS at 5 A/dm2

The average roughness profile (Ra) at 5 a/dm2 is 3.19 nanometres and the Root mean square deviation of the roughness profile (RMS) is 4.50 nanometers. The crystalline depth profile of zinc deposit from LTMS in the presence of aluminium chloride at 5A/dm2 is shown in fig.12 (C).

Surface topography investigations of zinc deposits from LTMS in a particular scanned area have shown the presence of granular, nodular ,platelet hcp crystal structure. The microstructure of zinc deposit vary from nanocrystalline to microcrystalline at different current densities.[22-26]

Conclusion: Nano crystalline adherent deposits of zinc with aluminium inclusion in the range of .4-.9% from imidazole with aluminium chloride electrolyte, could be obtained without any addition agent. The process is pollution free without using glove box .

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